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Synthesis of Macro-, Meso-, and Microporous Carbons from Natural and Synthetic Sources, and Their Application as Adsorbents for the Removal of Quaternary Ammonium Compounds from Aqueous Solution

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Macro- and mesoporous carbon samples have been prepared from both natural and synthetic sources. These natural and synthetic carbons (along with other microporous samples) have been characterized, with composition, thermal decomposition mode and stability (in inert and oxidizing atmospheres), and surface properties determined in each case. Order of thermal stability, porosity, and surface area have been determined, with carbons prepared from natural and synthetic sources exhibiting different thermal decomposition modes. Differences in surface area were attributed to differences in porosity, based on micropore and total pore volume. The adsorption of a series of quaternary ammonium (QA) compounds, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide, onto macroporous and microporous carbons was also investigated using Fourier transform infrared/attenuated total reflection spectroscopy. QA removal was found to increase with increase in carbon chain length, with results indicating that the nature of the carbon adsorbent (with respect to surface area and microporosity) had little influence on QA uptake. **© 1998 Academic Press**

Key Words: **macro-, meso-, and microporous carbons; surface area; pore size distribution; FTIR/ATR, quaternary ammonium compounds; adsorption.**

INTRODUCTION

Activated carbons are widely used as adsorbents in many adsorption–separation processes, with both small (laboratory) and large (industrial) scale applications being relatively commonplace. Activated carbons have, for example, been used as oral sorbents for the removal of uremic waste metabolites from the intestinal tract and as a support material in various catalytic processes (see for example 1–5). The high surface area of activated carbons, combined with their chemical inertness (toward heat in inert atmospheres for example) and their ability to endure harsh chemical environments (including highly acidic/basic and organic media), has resulted in considerable research interest in these types of materials. The ability of an activated carbon to act as an adsorbent or catalyst support depends then upon its structure, surface area, pore size/volume, and pore size distribution.

Macro- and mesoporous carbons are of considerable interest as adsorbents for the removal of bulkier organics from various industrial processes (6, 7). Microporous carbons, on the other hand, are useful as catalyst supports (5) and in chemisorption processes (6). From a commercial application point of view, the adsorption properties of activated carbons are of interest to alumina refiners. The removal of bulkier organics from the Bayer process (used for refining bauxite to smelting grade alumina) using activated carbon may provide alumina refiners with a suitable, cost effective, means of reducing the impact of these types of organics on the refining process.

Thus, taking into account the properties desirable in activated carbons, we have undertaken a systematic study of various carbons. This paper is primarily concerned with the preparation and characterization of heat-treated carbons obtained from natural and synthetic (artificial) sources and the ability of these carbons to remove Bayer active organic compounds from simple aqueous systems.

EXPERIMENTAL

Carbon Preparation

Heat-treated carbons were prepared from pure (100%) mustard oil, olive oil, almond oil, ghee (dehydrated butter), and camphor, as well as from mixtures of mustard oil and camphor (25%), olive oil and camphor (25%), almond oil and camphor (25%), and ghee and camphor (25%). Ghee is prepared from butter by removing its water content by

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TABLE 1
Sources and Elemental Analysis of the Carbon Samples

Sample code	Source	C (wt%)	H (wt%)	N (wt%)
C1	Mustard oil	90.2	1.0	0.05
C2	Olive oil	92.2	0.9	0.6
C3	Almond oil	88.8	0.9	0.2
C4	Ghee	93.3	0.9	0.4
C5	Camphor	92.9	1.8	0.3
C6	Mustard oil + camphor	90.7	1.2	0.1
C7	Olive oil + camphor	91.5	2.0	0.3
C8	Almond oil + camphor	92.9	1.0	0.7
C9	Ghee + camphor	92.3	1.3	0.1
C10	Commercial high surface area carbon	87.6	0.6	0.5
C11	Commercial high surface area carbon	88.8	0.9	0.3
C12	Commercial high surface area carbon	88.1	0.7	0.6

heating at a certain temperature for a certain period of time. In each case, the heat-treated carbon sample was prepared by controlled burning of the source at 900–1123 K for 5–6 h. The carbon samples C10, C11, C12 were all obtained commercially.

Characterization

All carbon samples were analysed for carbon, hydrogen, and nitrogen composition. Thermal analysis of the carbon samples, which were dried at 373 K in air for 24 h, was performed under inert and oxidizing atmospheres, using a fully automated computer-controlled Perkin–Elmer TGA7 thermal analyzer. Thermal analysis was performed using a sample mass of 5–6 mg and a platinum crucible sample holder. The temperature range employed was 303–1173 K, with a heating rate of 5 K min^{-1} and an atmosphere of nitrogen or air (flow rate = 100 $\mathrm{cm}^3\ \mathrm{min}^{-1}$). The BET surface area, pore volume, and nitrogen adsorption/desorption isotherms were obtained using a Micromeritics ASAP2000 surface area analyzer. Pore volume and pore size distribution were determined using the Barrett, Joyner, and Halenda (BJH) method (8). Each carbon sample was degassed at 473 K under vacuum for a minimum of 24 h.

Adsorption Experiments

Standard quaternary ammonium (QA) compound solutions (1.5 g/L; 50 mL) were added to heat-treated carbon samples (0.60 g), and the resultant slurry agitated (using an orbital shaker) for 2 h at room temperature. The supernatant was then separated from the solid carbon by means of gravity filtration, prior to analysis by Fourier transform infrared/attenuated total reflection spectroscopy (FTIR/ATR). Neat QA standard solutions and sample supernatant solutions (1000 μL) were simply pipetted into the ATR cell prior to spectral acquisition (as outlined below in the infrared measurements). QA compounds (dodecyltrimethylammonium bromide (QAC12), tetradecyltrimethylammonium bromide (QAC14), and hexadecyltrimethylammonium bromide (QAC16); ≈99%, Sigma–Aldrich Pty. Ltd., Castle Hill, New South Wales, Australia) were obtained commercially and used as received. All other reagents used were of AR grade and ultra-pure MilliQ water was used in all instances.

Infrared Measurements

Infrared spectra were acquired using a Perkin–Elmer System 2000 FTIR spectrometer equipped with deuterated triglycine sulfate (DTGS) and liquid-nitrogen-cooled mercury cadmium telluride (MCT) detectors. Spectra of the aqueous samples were the result of 1024 scans, acquired using the MCT detector at a resolution of 4 cm^{-1} and using a strong apodization function. All spectra were recorded using a Graseby Specac horizontal ATR accessory fitted with a ZnSe IRE (45°, 6 reflections), whose energy throughput was always optimized prior to spectral acquisition. All spectra were

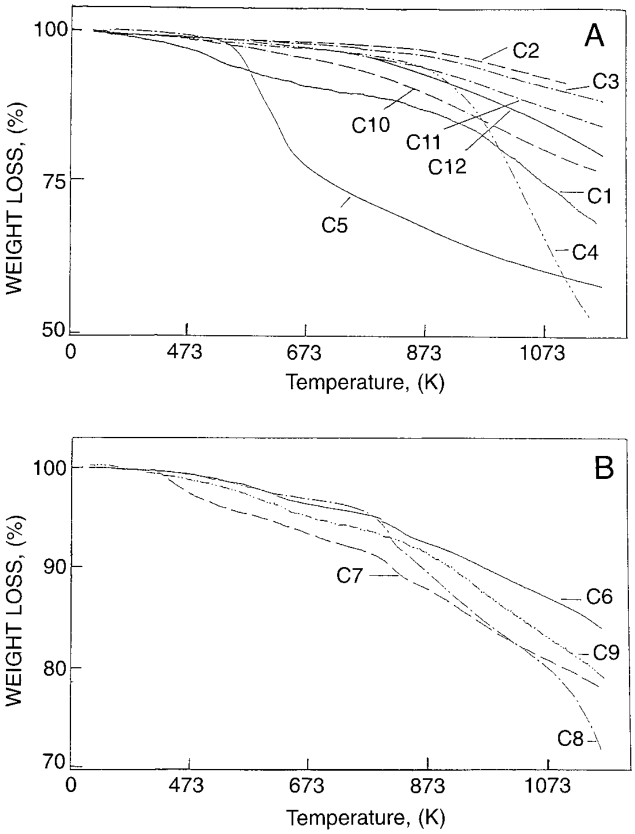

FIG. 1. Thermogravimetric curves for the decomposition of the carbon samples in nitrogen: (A) [C1, C2, C3, C4, C5, C10, C11] and (B) [C6, C7, C8, C9].

TABLE 2
Thermogravimetric Data of the Carbon Samples in Nitrogen

Sample	Weight loss (%) 303–723 K	723–823 K	823–923 K	923–1023 K	1023–1173 K	Total weight loss (%)
C1	9.8	1.6	2.9	6.2	10.9	31.4
C2	1.4	1.1	0.7	0.7	7.5	11.4
C3	2.3	1.1	1.2	1.9	11.4	17.9
C4	3.2	1.4	3.6	14.6	27.8	50.6
C5	25.5	4.8	4.0	3.7	4.1	42.1
C6	3.8	1.8	2.5	2.7	5.1	15.9
C7	7.0	2.7	3.6	3.8	4.9	22.0
C8	3.3	3.7	5.2	4.8	11.6	28.6
C9	5.3	1.5	2.8	4.6	6.4	20.6
C10	5.5	2.7	3.6	4.8	5.7	22.3
C11	3.2	1.8	2.3	3.2	4.1	14.6
C12	3.0	2.4	3.3	4.1	6.0	18.8

recorded with respect to the empty, energy-optimized, ATR accessory, and were corrected (for variation of penetration depth with wavelength) using the ATR correction algorithm incorporated in the Perkin–Elmer Spectrum software (all other spectral manipulations were also performed using this software package). No smoothing or baseline correction algorithms were used on any of the spectra presented.

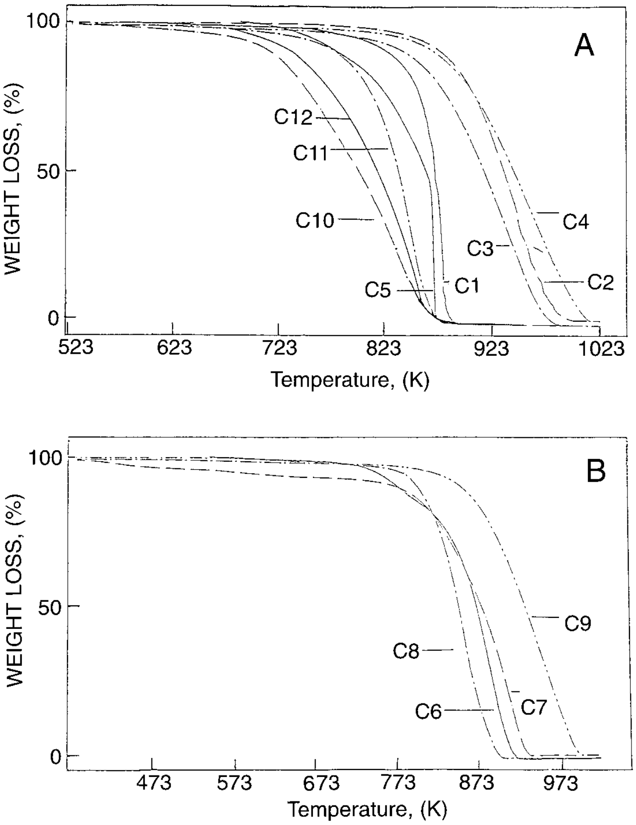

FIG. 2. Thermogravimetric curves for the decomposition of the carbon samples in air: (A) [C1, C2, C3, C4, C5, C10, C11] and (B) [C6, C7, C8, C9].

Spectra were, obviously, dominated by the strong infrared absorbance of water. Thus, in order to acquire a useful spectrum of the compound of interest, a reference spectrum was always subtracted from the sample spectrum. A water spectrum was thus subtracted from each sample spectrum (subtraction factor = 1.00 ± 0.05) yielding a spectrum of the sample in question.

RESULTS AND DISCUSSION

The carbon samples obtained from different sources, along with their sample code and carbon, hydrogen, and nitrogen analysis, are presented in Table 1. The carbon, hydrogen, and nitrogen contents vary from sample to sample and, subsequently, from source to source. The carbon sample prepared from ghee exhibited the highest carbon content, with the carbon content greater than 87.6% in all cases. Hydrogen content was found to be highest in the carbon sample prepared from a mixture of olive oil and camphor, whereas nitrogen was highest in the carbon sample prepared from the almond oil and camphor mixed source.

In order to investigate the thermal decomposition pattern of the different carbons, thermal gravimetric analysis was performed in inert and oxidizing atmospheres. Figure 1 (A, B) shows the thermogravimetric curves for the decomposition of the carbon samples prepared from single and mixed sources in nitrogen. It is interesting to note that the carbons prepared from natural and synthetic sources show different decomposition modes, with the total decomposition in the presence of nitrogen being in the range 14–51%. Thermogravimetric data obtained in different temperature ranges are

TABLE 3
Thermogravimetric Data of the Carbon Samples in Air

Sample	Weight loss (%) 303–723 K	723–823 K	823–923 K	923–1023 K	Total weight loss (%)
C1	1.4	7.3	91.3	—	100
C2	0.5	2.3	34.5	62.8	100
C3	1.8	4.0	49.5	46.9	100
C4	1.4	2.2	30	66.4	100
C5	1.4	22.2	76.4	—	100
C6	1.8	19.8	78.4	—	100
C7	6.8	14.1	74.6	4.5	100
C8	1.8	20.9	77.3	—	100
C9	1.8	4.2	39.5	54.5	100
C10	10.9	56.4	32.7	—	100
C11	3.2	32.3	64.5	—	100
C12	4.0	55.0	41.0	—	100

presented in Table 2. The carbon sample prepared from olive oil showed the least amount of thermal degradation in nitrogen atmosphere (with total weight loss of 11.4% at 1173 K), while the carbon prepared from ghee exhibited the maximum weight loss (around 51% at 1173 K). The C5 carbon (camphor source) exhibited a decomposition mode different from that exhibited by the other carbons prepared. The carbons prepared from mixed sources (C6, C7, C8, and C9) showed decomposition patterns similar to those of the single source carbons (C1, C2, C3, and C4).

The thermogravimetric decomposition curves of the prepared carbons in an oxidizing atmosphere (air) are presented in Fig. 2 (A, B). In an oxidizing atmosphere, the carbons prepared from natural and synthetic sources show different decomposition modes from those observed in an inert atmosphere. The observed total decomposition of the carbons in the presence of air is 100% in the temperature range 843–1023 K. Table 3 shows the thermogravimetric data obtained over different temperature ranges. In an oxidizing atmosphere, the carbon samples prepared from mustard oil (C1), olive oil (C2), almond oil (C3), ghee (C4), camphor (C5), mustard oil/camphor (C6), almond oil/camphor (C8), and ghee/camphor (C9) showed weight loss of less than 2% at 723 K. The carbon prepared from ghee showed the highest thermal stability in air, and complete thermal degradation was observed at 1014 K, while the carbon prepared from

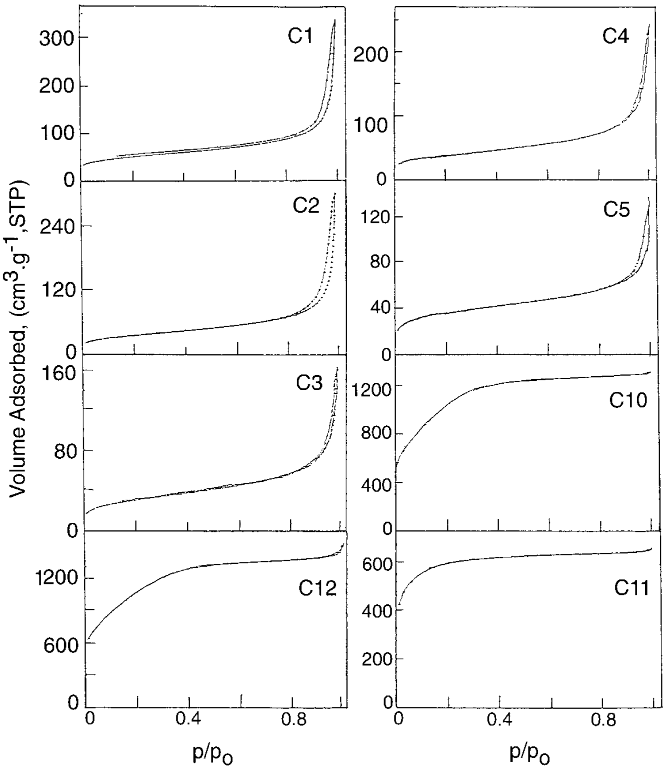

FIG. 3. Nitrogen adsorption/desorption isotherms for carbon samples.

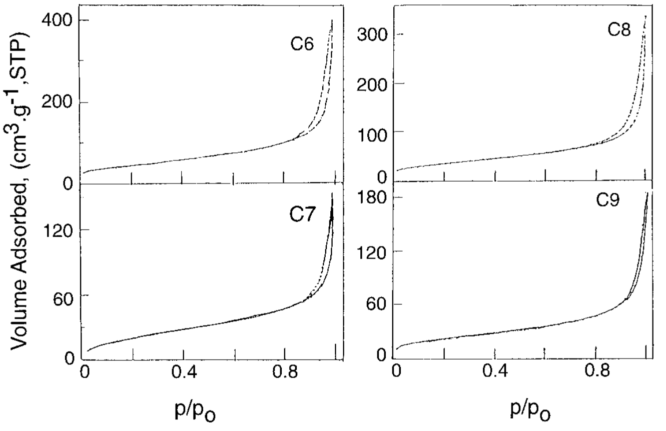

FIG. 4. Nitrogen adsorption/desorption isotherms for carbon samples prepared from the natural and synthetic mixtures.

TABLE 4
Surface Properties of the Carbon Samples

Sample	BET surface area (m^2 g^{-1})	External surface area (m^2 g^{-1})	Micropore surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Single point total pore volume of pores < [Å] (cm^2 g^{-1})	Average pore diameter (4V/A by BET) (Å)
C1	174	126	48	0.022	0.36 [1100 Å]	82.6
C2	123	103	20	0.009	0.34 [1114 Å]	109.4
C3	108	89	19	0.008	0.20 [1157 Å]	74.3
C4	131.7	116.3	15.4	0.0006	0.28 [1257 Å]	84.9
C5	128	101	27	0.011	0.16 [3205 Å]	51.4
C6	163.4	161.8	1.6	—	0.47 [1519 Å]	115
C7	76.5	76.3	0.2	—	0.17 [2044 Å]	87.9
C8	101	93.8	7.2	0.002	0.18 [1360 Å]	123
C9	84.4	84.3	0.1	—	0.22 [1319 Å]	106
C10	3880	—	—	—	2.05 [1616 Å]	21
C11	2062	776	1286	0.59	1.02 [2286 Å]	14.7
C12	3940	—	—	—	2.24 [1411 Å]	22.7

camphor showed the lowest thermal stability in air. The order of thermal stability of the carbon samples in air was found to be C5 < C10 = C12 < C11 < C1 < C8 < C6 < C7 < C3 < C9 < C2 < C4. Of the carbons prepared from mixed sources, C9 (ghee/camphor) exhibited the highest decomposition temperature.

The nitrogen adsorption–desorption isotherms for the carbon samples are shown in Figs. 3 and 4. The BET surface area, external and micropore surface area, micropore volume and total pore volume for the carbons investigated are listed in Table 4. Nitrogen adsorption at 77 K by the carbons prepared from mustard (C1), olive (C2) and almond (C3) oils, ghee (C4), camphor (C5), and mixed sources (C6–C9) leads to type IV isotherms (Figs. 3 and 4). The isotherms for the C10, C11, and C12 carbons (Fig. 3) show very high nitrogen uptakes in comparison to other carbon samples. This indicates the presence of some porosity, and comparison of the isotherms for C11, C10, and C12 carbons with those for C1–C9 carbons suggests that this porosity is present at relatively high levels.

For the C1–C9 carbons, the surface area and total pore volume varies in the range 84–174 m^{2}g^{-1} and 0.2–0.5 cm^{3}g^{-1}, respectively. Comparison of the BET results indicates that the surface area and pore volume of the carbons

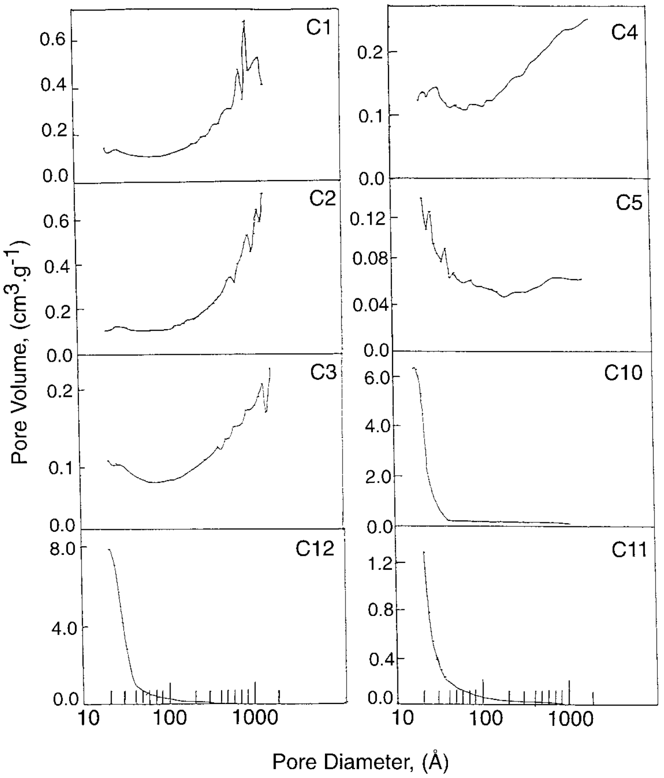

FIG. 5. The pore volume distributions (adsorption) for carbon samples.

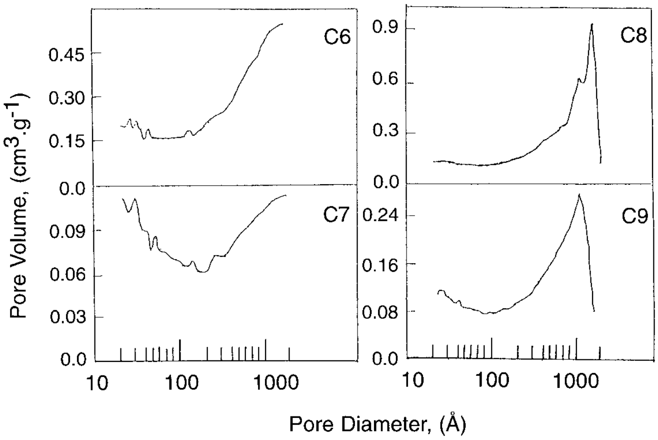

FIG. 6. The pore volume distributions (adsorption) for carbon samples prepared from the natural and synthetic mixtures.

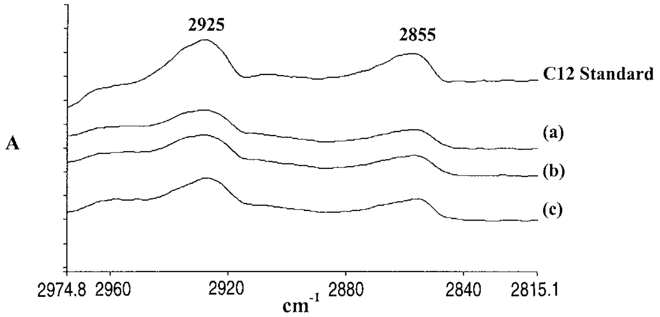

FIG. 7. FTIR/ATR spectra of aqueous QAC12 solutions after exposure to C3, C10, and C1 heat-treated carbons.

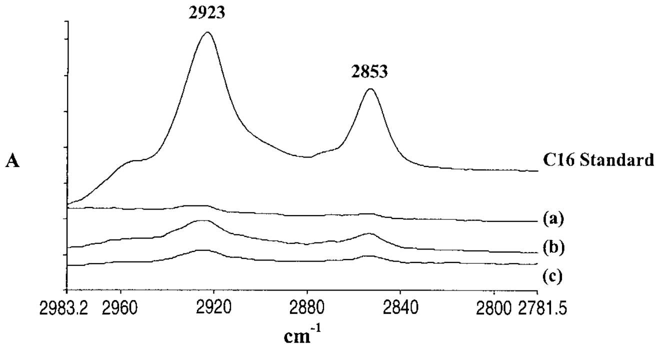

FIG. 9. FTIR/ATR spectra of aqueous QAC16 solutions after exposure to C3, C10, and C1 heat-treated carbons.

prepared from mixed sources (C6–C9) are lower than those for the carbons prepared from a single source (C1–C5). The order of porosity and surface area for the carbon samples is as follows: C12 > C10 >> C11 >>>> C1 > C6 > C4 > C5 > C2 > C3 > C8 > C9 > C7. For the C1, C2, and C5–C8 samples, the hysteresis loop is well pronounced, while for the C3, C4, and C9 carbons, it is noticeable. In these carbon samples, the hysteresis loop can be classified as H3 according to the IUPAC recommendation (9). It is interesting to note that the hysteresis loop is not noticeable for the C10, C11, and C12 carbons. These samples possess very high surface areas (3880, 2062, and 3940 m^2g^{-1}, respectively) and are therefore expected to be highly porous.

The BET surface areas of the samples range from 70 to 3950 m^2g^{-1}. The differences in the surface areas can be attributed to the differences in porosity on the basis of the micropore volume and the total pore volume. Samples C2–C9 are less porous than C1, whereas C11 and especially C10 and C12 are considerably porous. The pore size distributions obtained by BET are presented in Figs. 5 and 6. The C1–C9 carbon samples possess a small number of pores, mostly in the macropore and mesopore regions, with their microporosity correspondingly low. The distribution of pores in these samples is nonuniform. On the other hand, the C10–C12 carbon samples are microporous, with a very small fraction of meso- and macro- pores evident. A uniform pore distribution is observed in these samples.

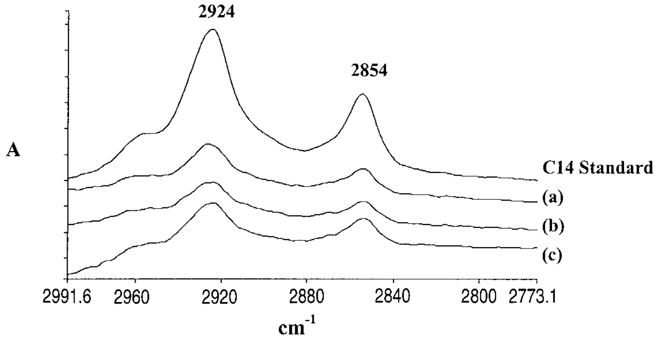

FIG. 8. FTIR/ATR spectra of aqueous QAC14 solutions after exposure to C3, C10, and C1 heat-treated carbons.

Adsorption of Quaternary Ammonium Compounds

The adsorption of the series of quaternary ammonium compounds QAC12, QAC14, and QAC16 over the C1, C3, and C10 heat-treated carbons was investigated using FTIR/ATR. This study was conducted in order to observe the effect of surface area and pore size of the carbon on the removal of the relatively large quaternary ammonium compounds from aqueous solution. Three carbons were selected, two samples with low surface area and macro- and mesopores, with the third sample highly microporous and having a large surface area. The FTIR/ATR aqueous spectra of the C–H stretching region of the QAC12, QAC14, and QAC16 compounds can be seen in Figs. 7–9. The two strong bands around 2925 and 2855 cm^{-1}, in the QAC12, QAC14, and QAC16 spectra, were assigned to the asymmetric and symmetric CH_2 stretching vibrations of the methylene chain, respectively, while the two weaker bands, evident around 2955 and 2875 cm^{-1}, were assigned to the R–CH_3 asymmetric and symmetric stretching vibrations, respectively. These assignments are in good agreement with the literature (10–13). No other bands were discernible in the ATR spectra obtained.

Difference spectra (water subtracted) of each of the standard QAs and respective carbon-treated QA solutions can be seen in Figs. 7, 8, and 9. The percentage of QA removal was determined based upon the principal of solution depletion. Peak areas of the asymmetric and symmetric CH_2 stretching vibrations were determined (in each case) for the relevant QA standard and for the supernatant sample after equilibration with heat-treated carbon. Percentage of QA removal was then calculated by expressing the difference between standard and sample peak areas as a percentage of the standard peak area, for both the asymmetric and the symmetric stretching vibrations. The average of these two values was then taken to obtain an average percentage of removal of each QA, for each carbon tested (see Table 5). The C10 carbon sample showed the highest removal of QAs from aqueous solution. The amount of QA removed by the C1, C3, and C10 carbons was found to increase with an increase in the molecular weight (carbon chain length) of the QA compounds. The FTIR/ATR results indicate that the presence of high surface area and microporosity does not have much influence on the removal of large, bulkier organic molecules.

TABLE 5

Removal of Quaternary Ammonium [QA] Compounds from Aqueous Systems by Heat-Treated Carbon Samples

Heat-treated carbon	% QA removal		
	QAC12	QAC14	QAC16
C1	42	64	93
C3	44	69	97
C10	46	73	98

Note. Dodecyltrimethylammonium bromide (QAC12), tetradecyltrimethylammonium bromide (QAC14) and hexadecyltrimethylammonium bromide (QAC16).

CONCLUSIONS

Various types of carbons (exhibiting low and high surface areas) obtained from natural and synthetic sources, show different composition, thermal stability (in nitrogen and air), surface area, and porosity. Meso- and macroporous carbons can be prepared from mustard oil, olive oil, almond oil, ghee, and camphor. The thermal stability, surface area, and pore size distribution vary for carbon samples prepared from single and mixed sources. The low surface area carbons with meso- and macropores effectively remove large, bulky QAs from aqueous solution.

REFERENCES

1. Bansal, R. C., Donnet, J.-B., and Stoekli, F., ‘‘Active Carbon.’’ Dehker, New York, 1988.
2. Koide, K., *Jinko Zoki* **16,** 1193 (1987).
3. Tamai, H., Sumi, T., and Yasuda, H., *J. Colloid Interface Sci.* **177,** 325 (1996).
4. Koide, K., Koshikawa, S., Yamane, Y., and Hidaka, S., *Nihon Rinsho* **49,** 758 (1991).
5. Gallezot, P., Laurain, N., and Isnard, P., *Appl. Catal. B: Environment* **9,** L11–L17 (1996).
6. Dargaville, T. R., Guerzoni, F. N., Looney, M. G., and Solomon, D. H., *J. Colloid Interface Sci.* **182,** 17 (1996).
7. Rochester, C. H., and Strachan, A., *J. Colloid Interface Sci.* **177,** 339 (1996).
8. Barrett, E. P., Joyner, L. S., and Halenda, P. P., *J. Am. Chem. Soc.* **73,** 373 (1951).
9. Kruk, M., Jaroniec, M., and Bereznitski, Y., *J. Colloid Interface Sci.* **182,** 282 (1996).
10. Teng, H., and Suuberg, E. M., *J. Phys. Chem.* **97,** 479 (1993).
11. Hind, A. R., Bhargava, S. K., and Grocott, S. C., *Langmuir,* **13,** 3483 (1997).
12. Kung, K-H. S., and Hayes, K. F., *Langmuir,* **1993,** 9, 263.
13. Weers, J. G., and Scheuing, D. R., *in* ‘‘Fourier Transform Infrared Spectroscopy in Colloid and Interface Science,’’ ACS Symposium Series, Vol. 447. Am. Chem. Soc., Washington, DC, 1991.